

Coexistence of Lewis Acid and Base Functions: A Generalized View of the Frustrated Lewis Pair Concept with Novel Implications for Reactivity

Heinz Berke, Yanfeng Jiang, Xianghua Yang, Chunfang Jiang, Subrata Chakraborty, and Anne Landwehr

Dedicated to Nobel Laureate Roald Hoffmann on the occasion of his 75th birthday

Abstract Sterically congested Lewis pairs cannot form Lewis adducts; instead they establish encounter complexes of “frustrated” Lewis pairs (FLPs). These encounter complexes have recently been recognized to be capable of activating, i.e., splitting, homopolar and polar single and double bonds, which rendered a new reactivity principle. With the help of qualitative orbital considerations this chapter reviews and explains the reactivity of FLPs toward homopolar $Z-Z$ or $Z-Z'$ single bonded molecules, such as $H-H$ and $C-H$ single bonds, assuming in the encounter complexes the action of strongly polarizing Coulombic fields originating from the FLP constituents. This reactivity principle has been extended in its view to the activating potential for homopolar $Z-Z$ or $Z-Z'$ single bonds of strongly polarized $[X-Y \leftrightarrow X(+)-Y(-)]$ σ and $[X=Y \leftrightarrow X(+)-Y(-)]$ π bonded molecules ($X, Y =$ atoms or molecular fragments; electronegativity of $X <$ electronegativity of Y). A striking analogy in the reaction behavior of FLPs and strongly polarized σ and π bonded molecules could be revealed based on the analyses of selected examples of “metal-free” (main group element reactions) or metal-based (containing transition metals) σ bond metathesis reactions and σ bond additions of H_2 and alkanes to polarized main group element and metal to ligand π bonds. Related to the described polar reaction types are Z, Z' double atom or group transfers between highly polarized double bonds of XY and $X'Y'$ molecules combining a Z, Z' elimination with an addition process. Multiple consecutive Z, Z' double atom or group transfers are denoted as double H transfer cascade reactions. Analyzed by examples

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are concerted or stepwise double H transfers and double H transfer cascades with $Z, Z' = H, H$ from the “metal-free” and metal-based realms: the Meerwein–Pondorf–Verley reduction, H,H exchanges between amine boranes and between amine boranes and unsaturated organic compounds, and the crucial H,H transfer steps of Noyori’s bifunctional and Shvo type transfer hydrogenation catalyses.

Keywords σ Bond metathesis · Bifunctional catalysis · C–H activation · Double H transfer · Double H transfer cascade · Frustrated Lewis pair · H_2 activation · Hydrogenation · Meerwein–Pondorf–Verley reduction · Metal-free hydrogenation · Transfer hydrogenation

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1 Prologue

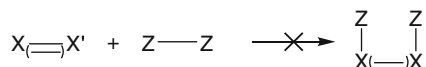
Building bridges in chemistry was one of the great challenges Roald Hoffmann conveyed to the scientific community. Indeed, this idea became a rich source of chemical creativity never running dry on the exploitation of analogies and synergisms. “Similar but not the same” stood for the isolobal analogy and was one of the soft principles behind the bridge building reconciling and embedding extremes of chemistry into unified views. But how about an opposite strategy to foster extremes and bringing real chemical antagonists together; could one generate benefaction by forcing them to coexist? For instance, highly charged anions side by side with highly charged cations, a proton source side by side with a base, a reducing center side by side with an oxidizing center and eventually a Lewis acidic center side by side with a Lewis basic center, could this ever work out fine, and even more can coexistence of antagonists be a source of creation in chemistry and maybe in science in general? The message from this chapter will be: Yes, they can! But antagonists must be tuned for their tasks first and go through a phase of “frustration” before one had learned how they can contribute beneficially to creation.

2 Generalized Aspects of Bond Activations by Polarized Molecular Arrangements

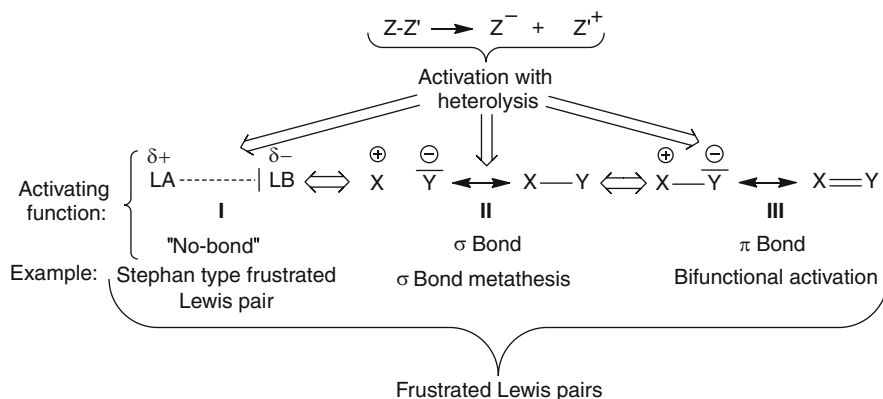
2.1 σ Bond Activation of Small Molecules by 1,2-Addition

In the context of this chapter σ bonds are referred to as strongly covalent σ bonds of generalized molecules with homopolar $Z-Z$ bonds (Z = atom or molecular fragment; $Z-Z$, for instance C–C bonds or H–H bonds) or with nearly homopolar $Z-Z'$ σ bonds (Z, Z' = atoms or molecular fragments of low electronegativity difference; $Z-Z'$, for instance C–H bonds). σ Bond activation of small molecules includes their preparation for bond splitting and their splitting process. σ Bond splittings are generally difficult chemical tasks due to the high bond strengths normally involved. In particular in organic chemistry such strong bonds also often lack appropriate kinetic transformation pathways. Initial homolytic $Z-Z$ or $Z-Z'$ σ bond splitting and subsequent fragment addition to molecules is normally not a practical reaction alternative. Indeed facile splitting of strong covalent homopolar σ bonds of the $Z-Z$ type or splitting of nearly homopolar $Z-Z'$ σ bonds can only be accomplished when bond breaking is combined with bond making processes. New principal transformations including σ bond splitting and bond making would be expected to add greatly to the potential of valuable synthetic strategies to construct complex molecular topologies in atom efficient ways.

However, quite simple pathways for concerted transformations of $Z-Z$ or $Z-Z'$ molecules to be added to homopolar $X-X$ σ or $X=X$ π bonding systems are not



Scheme 1 Failure of homopolar Z-Z σ bond activation utilizing for energetic compensation a simultaneous 1,2-addition process to homopolar X-X and X=X σ and π bonded systems. As single-step reactions they constitute thermally symmetry forbidden $2e + 2e$ processes



Scheme 2 Comparative sketch of the Z-Z' heterolytic activation by the "no-bond" [LA $\cdots$ LB] arrangement **I** or by the strongly polarized σ and π bonded arrangements **II** and **III**, respectively. LA Lewis acid, LB Lewis base. X,Y = generic descriptors for atoms or molecular fragments. Electronegativity of X < electronegativity of Y was deliberately set as given. All arrangements **II** and **III** are expected to behave chemically related to frustrated Lewis pairs (FLPs) capable of inducing Z-Z' heterolytic splitting and subsequent addition to LA and LB or X and Y

available as thermal processes. A high activation barrier with unfavourable kinetics is expected for a combined single-step reaction since, according to the conservation of orbital symmetry rules, such molecular conversions would be thermally forbidden $2e + 2e$ processes (Scheme 1).

A way out of the given dilemma would be the utilization of superimposition of strong Coulomb fields originating from for instance the XY reaction partners polarizing the Z-Z or Z-Z' σ bonds to assist their heterolytic splitting. Such characteristics are apparently inherent to the reaction courses of frustrated Lewis pairs [LA $\cdots$ LB] (FLPs) (LA = Lewis acid, LB = Lewis base) discovered by the Stephan group in 2006 [1] denoting them also as Stephan type FLPs. In Scheme 2 the FLPs are also described as "no-bond" arrangements **I** functioning as encounter complexes with their Lewis constituents to possess huge separations of about 4–5 Å, which naturally has the consequence of having no covalent bond between them. However, these arrangements keep contact between the face-to-face oriented Lewis components. Among the forces to hold LA and LB together the electrostatic field plays the major role. As indicated, it is the electrostatic field between the Lewis components which is expected to enforce heterolytic bond splittings of σ and other types of bonds, which became further substantiated in the elegant theoretical

analysis of Grimme and Erker [2]. The main condition for FLP formation is that the Lewis pair must be “frustrated” preventing Lewis pair bond formation by steric congestion and concomitantly preventing also “quenching” of the FLPs physical and chemical properties. Such contact pairs of arrangement **I** function as kinetically important transients inducing at a later stage of the reaction course the splitting of embraced small $Z-Z$ and $Z-Z'$ σ bonded molecules (it should be noted that π bonded $Z=Z$ and $Z=Z'$ molecules can also be split, but we will not treat this aspect in this chapter).

In extension of the FLP perspective, it is the main idea of this chapter to demonstrate that various types of strongly polarized $[X-Y \leftrightarrow X(+)-Y](-)$ σ and $[X=Y \leftrightarrow X(+)-Y](-)$ π bonded molecules (X, Y = atoms or molecular fragments; electronegativity of $X <$ electronegativity of Y), denoted in Scheme 2 as arrangements **II** and **III**, can indeed behave like Stephan type FLPs and split homopolar $Z-Z$ or nearly homopolar $Z-Z'$ σ bonds. In the following sections of this chapter we will restrict the generic description for σ bonded molecules to the $Z-Z'$ notation of nearly homopolar σ bonds, which is expected to include the homopolar $Z-Z$ case, unless there is very special need to emphasize this case. As for the Stephan type FLPs, the splitting reactions induced by arrangements **II** and **III** should occur with $Z-Z'$ heterolysis and formation of polar σ bonds to X and Y .

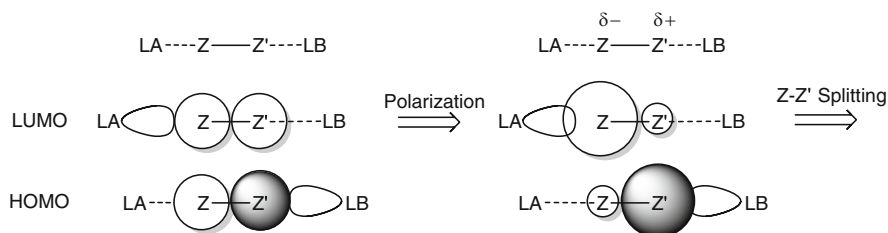
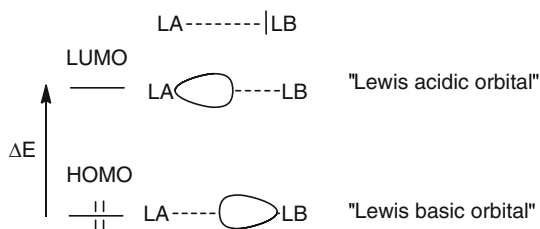
As demonstrated in Scheme 2 the arrangements **I–III** are related by the coexistence of Lewis acidic and Lewis basic centers. These centers cannot be neutralized or “quenched” by Lewis acid/base reactions. Their chemical fate is to stay “frustrated”. In the Stephan type FLPs the frustration effect is expressed by the inability to combine the Lewis pairs to form donor/acceptor bonds. For the $[X-Y \leftrightarrow X(+)-Y](-)$ σ bonded systems **II** and the $[X=Y \leftrightarrow X(+)-Y](-)$ π species **III** the frustration aspect is electronically derived by the inability to access the double bonded canonical forms and the pre-eminence of the polarized canonical forms.

2.2 Qualitative Orbital Views for the Heterolytic Activation of Homopolar $Z-Z'$ σ Bonds by the Arrangements **I–III**

A generalized frontier orbital picture of the Stephan type FLP reaction mode (Scheme 3) emphasizes the fact that HOMO and LUMO representing the “Lewis basic” and the “Lewis acidic” orbitals are naturally highly localized at the LA or LB centers; this is because of the long distance between these centers in the encounter complexes, which prevents covalent orbital interactions. The “Lewis acidic” orbital is expected to be positioned at relatively higher energies than that of the “Lewis basic” orbital. The HOMO/LUMO gap ΔE goes in first order approximation along with the strengths in Lewis acidity and basicity. Strong Lewis pairs are expected to have small ΔE s and vice versa.

The splitting of small molecules in the gap of an FLP is in the initial phase of the activation process considered not to proceed by orbital control but by polarization

Scheme 3 Schematic frontier orbital picture of an FLP at contact distance revealing no covalent bond interaction and a picture of localized orbitals for LA and LB



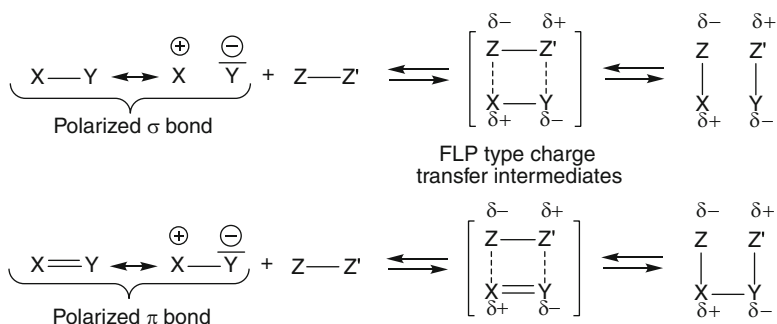
Scheme 4 Schematic representation of the polarization of a Z-Z' σ bond induced by the electrical field between LA and LB in interaction with the frontier orbitals of an FLP

of the ZZ' σ bonds exerted by the electrical field originating from the Lewis pair, which is supposed to lift restrictions from covalency or from the conservation of orbital symmetry principle (Scheme 4).

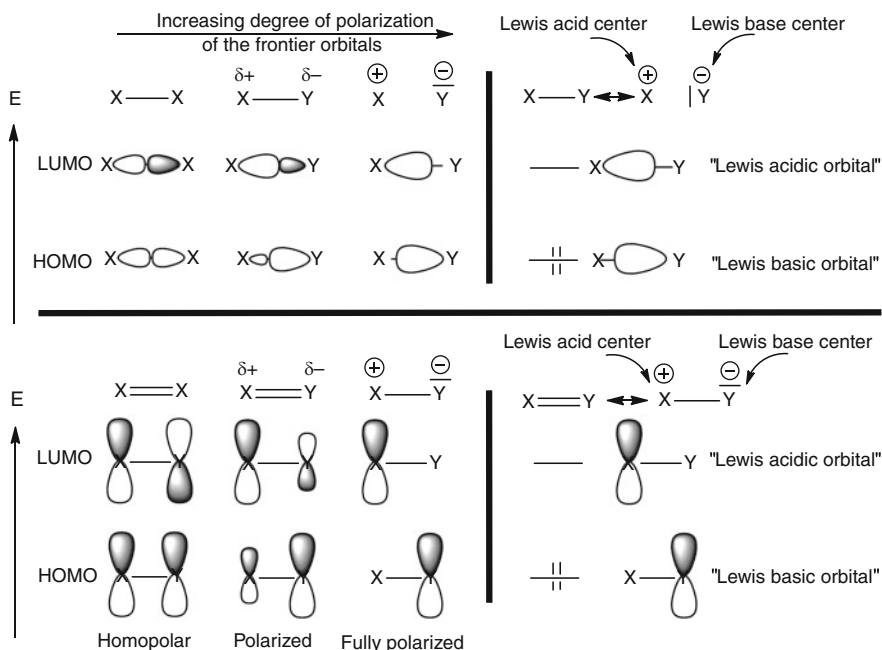
This polarization will assist the subsequent splitting process by preparation of the crucial Z-Z' frontier orbitals for better overlap with the LA and LB orbitals for the orbital controlled phase of the reaction course. The main general conclusion from this discussion on Stephan type FLPs is therefore that FLP activation of small molecules will be facilitated by generation of strongly polar environments and this knowledge is taken as the main message for the comparison with σ bond activations by highly polarized σ and π bonds discussed in the following sections.

As discussed in the previous section, highly polarized $[X-Y \leftrightarrow X(+)-Y(-)]$ σ bonded and $[X=Y \leftrightarrow X(+)-Y(-)]$ π bonded molecules as depicted in Scheme 5 ought to enable activation of Z-Z' σ bonds (and also Z=Z' π bonds, although not being a subject of discussion in this chapter). In reality both reactions are expected to be reversible furnishing 1,2-elimination processes.

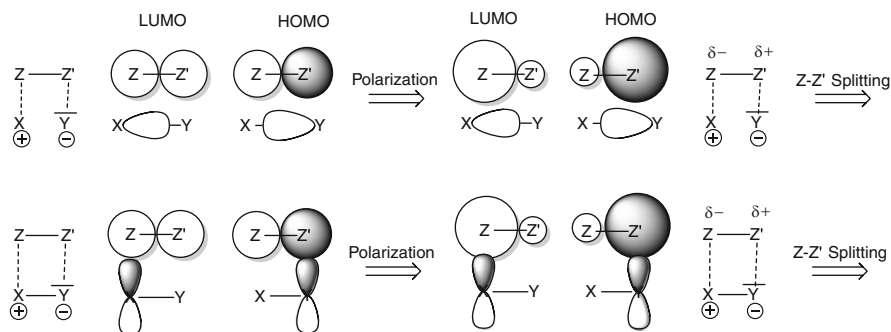
In contrast to the Stephan type FLP reactions, which have linearly or nearly linearly arranged intermediates (Scheme 3), the activation processes of Z-Z' molecules induced by $[X-Y \leftrightarrow X(+)-Y(-)]$ σ bonded and $[X=Y \leftrightarrow X(+)-Y(-)]$ π bonded molecules are expected to pass through four-membered cyclic charge transfer intermediates (Scheme 5). The frontier orbital features of these intermediates however resemble those of Scheme 4. As emphasized before, the physical cause for the analogy in reactivity is expected to originate mainly from strong Coulombic fields created by the polarity of the $[LA \cdots LB]$ arrangement or of the XY species polarizing the Z-Z' substrate's σ bonds. Scheme 6 (top) details in generalized form the frontier orbital picture of Z-Z' σ bond activations occurring as



Scheme 5 General scheme for the activation of σ bonds of small $Z-Z'$ molecules by strongly polarized XY σ (*top*) and π bonds (*bottom*) demonstrating via four-membered cyclic charge transfer intermediates FLP behavior with $Z-Z'$ splitting. $X, Y, Z, Z' =$ atoms or molecular fragments. Electronegativity of $X <$ electronegativity of Y



Scheme 6 Left: schematic representation of the frontier orbitals of homopolar and polarized σ (*top*) and π bonds (*bottom*) with increasing degrees of polarization. Right: qualitative molecular orbital diagram of the HOMO and LUMO and of strongly polarized XY σ (*top*) and π (*bottom*) bonds emphasizing the coexistence of Lewis acidic and basic centers. Electronegativity of $X <$ electronegativity of Y

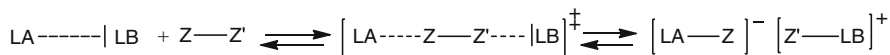


Scheme 7 Frontier orbital scheme for the attack of a $Z-Z'$ σ bonded molecule to XY σ and π type molecules without effect from polarization (*left*) and for the attack with support from polarization via the action of strong Coulomb fields (*right*) inducing eventually $Z-Z'$ splitting. Electronegativity of $X <$ electronegativity of Y

1,2-additions to polarized $[X-Y \leftrightarrow X(+)-Y(-)]$ σ bonds and Scheme 6 (bottom) details the corresponding reaction with $[X=Y \leftrightarrow X(+)-Y(-)]$ π bonds. Both reactions are expected to possess in the highly polarized forms distinctly localized Lewis acidic and Lewis basic centers in the X and Y molecular fragments. These centers increase in Lewis acid and base strength along with the degree of polarization of the XY frontier orbitals as shown on the left side of Scheme 6, and are dependent on the electronegativity differences of the X and Y groups. The saturated products of these processes are expected to possess polar $Z(\delta^-)-X$ and $Z'(\delta^+)-Y$ bonds.

Based on the frontier orbital shapes the central lateral approach of a $Z-Z'$ σ bonded molecule, a homopolar molecule, or a molecule of low polarity (low electronegativity difference for Z and Z') onto highly polarized XY σ and π bonded molecules would show in the models of the charge transfer intermediates of Scheme 5 inappropriate binding matches. The same is valid for the ZZ' approach to Stephan type FLPs. In a first order approximation the HOMOs of both types of the XY molecules are expected to interact with the σ^* LUMO of ZZ' and, vice versa, the LUMOs of XY with the σ HOMO of ZZ' . As sketched in Scheme 7 the HOMO/LUMO orbital misfits would be due to the incompatibility of the highly localized XY orbitals and the delocalized σ bond orbitals of the $Z-Z'$ molecules. This discrepancy is being lifted by polarizing the $Z-Z'$ σ bond when the XY moieties are approached.

Based on the acquired general knowledge of a qualitative orbital picture for the splitting modes of homopolar $Z-Z'$ molecule at highly polarized arrangements, real examples of $Z-Z'$ splitting reactions by $LA \cdots | LB$ type **I** and XY type **II** and **III** systems will be discussed in the following Sects. 3 and 4.



Scheme 8 General scheme for the heterolytic splitting of ZZ' σ bonds via Stephan type FLP activation. *LA* Lewis acid, *LB* Lewis base. Z, Z' = atoms or molecular fragments

3 Z–Z' σ Bond Activation by “No-Bond” Arrangements (Stephan Type FLPs) and by Highly Polarized $[\text{X}-\text{Y} \leftrightarrow \text{X}(+) \text{Y}(-)]$ σ and $[\text{X}=\text{Y} \leftrightarrow \text{X}(+)-\text{Y}(-)]$ π Bonds

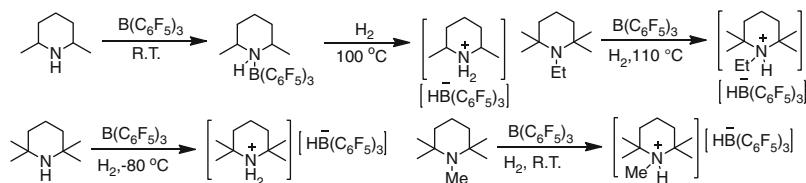
3.1 Stephan Type FLPs Representing Polar “No-Bond” Arrangements of Type I in Z–Z' σ Bond Activations

In order to allow for better comparisons we would like to detail in this chapter the introductory description of the properties of Stephan type FLPs with $[\text{LA} \cdots | \text{LB}]$ standing for the “no-bond” arrangements **I** of Scheme 2. It became meanwhile an established fact that Stephan type FLPs are very powerful chemical tools to split σ bonds (and also π bonds) causing their heterolysis (Scheme 8) [3]. Balancing electrons these reactions proceed as $2e + 2e$ transformations of two pairs of electrons from LB and from the $\text{Z}-\text{Z}'$ σ bond. They are converted into the new bonds of the Z or Z' atoms or fragments to LA and LB, but bear the principal character of symmetry forbidden $2e + 2e$ additions, also applicable to the cases of their reverse reactions: $2e + 2e$ 1,2-eliminations. Such thermally induced processes with transformation of homopolar covalent bonds are expected to possess high activation barriers. However, the 1,2-addition reactions are often reversible with low activation barriers or are in equilibrium, also enabling eliminations of the $\text{Z}-\text{Z}'$ species from the LA and LB polar σ bonded states (Scheme 2).

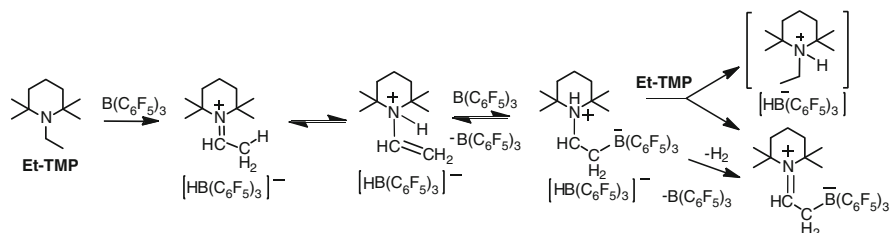
3.2 Examples of Z–Z' Splitting by Stephan Type FLPs

Since the discovery of FLPs and their reactions by Stephan in 2006 [1], a great variety of examples has demonstrated versatility of the reactions to split $\text{Z}-\text{Z}'$ molecules. For the majority of cases H_2 was chosen as the homopolar $\text{Z}-\text{Z}'$ component. Cases of FLP activations of other homopolar molecules, like alkanes, are as yet not known. The FLPs were either so-called “linked” ones, where the Lewis acid LA and the Lewis base LB are bridged by organic units or are “free” Lewis pairs. These many examples of H_2 activation were comprehensively reviewed in the article of Stephan and Erker [3] but will not be repeated here.

FLP heterolytic splitting of H_2 will be exemplified by reactions studied in our group [4–7]. We studied systematic variations of the Lewis base and Lewis acid strengths of FLPs and their steric congestions. Dimethyl piperidine, tetramethylpiperidine, *N*-methyl tetramethylpiperidine, *N*-ethyl tetramethylpiperidine, several



Scheme 9 FLP reaction of piperidine derivatives with BCF and H_2



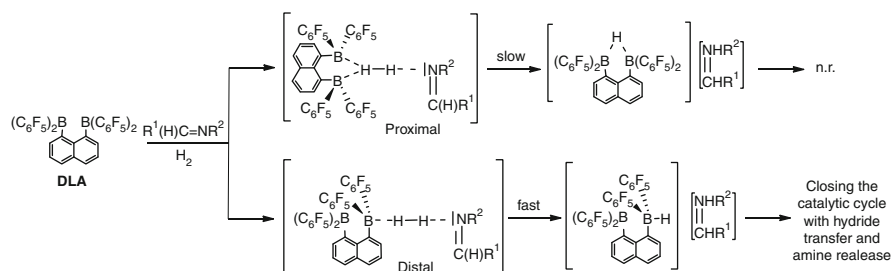
Scheme 10 Reaction course of *N*-ethyl tetramethyl piperidine with BCF at room temperature

sterically hindered pyridines and tri(*tert*-butyl)phosphine were applied as Lewis bases and $B(C_6F_5)_3$ (BCF) and $RB(C_6F_5)_2$ ($R = C_6H_{11}$ and CH_2CH_2Ph) as Lewis acids. In this context it is perhaps interesting to mention that the LUMO of BCF is at -3.81 eV, while the HOMOs of tetramethylpiperidine or tri(*tert*-butyl)phosphine are at -5.22 and -5.41 eV, respectively, showing a reasonable energetic separation as an electronic pre-condition to establish polarization in “no-bond” arrangements of type **I** as demonstrated in Scheme 4.

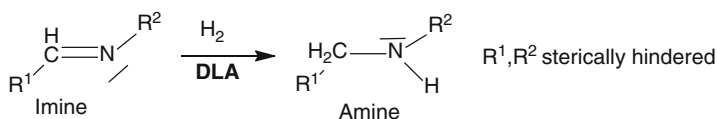
An account of our FLP type studies will be presented here. For instance the reactions of a series of piperidine derivatives with BCF and H_2 (Scheme 9) furnished FLP splitting, but required quite different initiation temperatures. For the two Lewis bases dimethylpiperidine and *N*-ethyl tetramethylpiperidine $100^\circ C$ or more had to be applied, while for tetramethylpiperidine and *N*-methyl tetramethylpiperidine room temperature or below turned out to be enough.

Dimethylpiperidine and *N*-ethyl tetramethylpiperidine turned out to be special cases in that the former produces Lewis adducts, which can dissociate for FLP reactions only at elevated temperatures, and the latter showed different reaction patterns at room temperature with initial hydride abstraction by BCF at the α carbon atom of the ethyl group, then a 1,3-H-shift occurs to form a piperidinium ion, which after BCF addition undergoes two kinds of deprotonation (Scheme 10).

Another example from our group concerns a catalytic study of imine hydrogenation catalyzed using the double Lewis acid (DLB) 1,8-bis(dipentafluorophenyl)borylnaphthalene. The imines play the role of a substrate and at the same time the Lewis base required for the FLP function, which has to be sterically hindered. Therefore only imines with some degree of steric congestion could be hydrogenated as depicted in the table below.



Scheme 11 Sketch of the FLP formation with **DLA** and imines via proximal and distal approaches

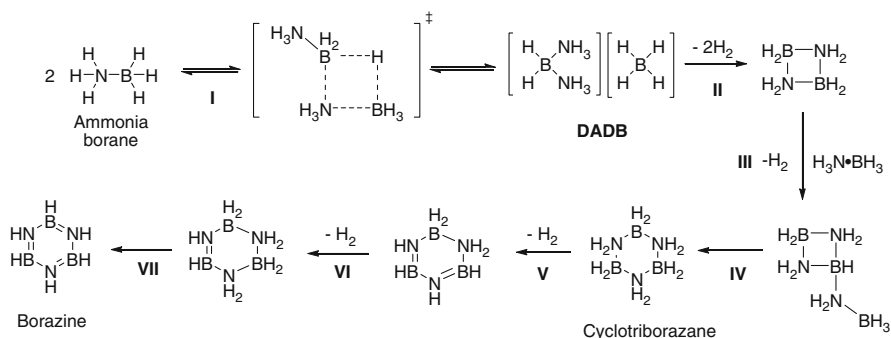


Imine	<i>t</i> (h)	Amine	Yield (%)	TOF
PhCH=NCHPh ₂	1	PhCH ₂ NHCHPh ₂	>99	20/h
PhCH=N <i>t</i> Bu	1	PhCH ₂ NH <i>t</i> Bu	>99	10/h
PhCH=NPh	1	PhCH ₂ NHPh	78	8/h
PhCH=NCH ₂ Ph	6	PhCH ₂ NHCH ₂ Ph	<5	
PhCH=NC ₆ H ₄ Cl- <i>p</i>	1	PhCH ₂ NHC ₆ H ₄ Cl- <i>p</i>	>99	10/h
<i>p</i> -ClC ₆ H ₄ CH=NC ₆ H ₄ Cl- <i>p</i>	1	<i>p</i> -ClC ₆ H ₄ CH ₂ NHC ₆ H ₄ Cl- <i>p</i>	>99	10/h
<i>p</i> -NO ₂ C ₆ H ₄ CH=NPh	1	<i>p</i> -NO ₂ C ₆ H ₄ CH ₂ NHPh	>99	10/h

The mechanism of this reaction has been studied in quite some detail, revealing that the initial step is FLP formation with H₂ heterolysis. Apparently the approach of the H₂ molecule to the boron centers can occur in two different ways: proximal to one or both centers at the same time or distal, making contact with only one center (Scheme 11). Due to steric hindrance the proximal approach is presumed to be slower than the distal one. The latter pathway is even expected to prevail in the catalytic cycle dominating then amine formation. The proximal approach to **DLA**, which could provide much higher Lewis acidity, should not be available kinetically in such hydrogenation catalyses.

In separate experiments it could be shown that the internally bridged diborohydride does not react with iminium cations, presumably also due to a too strong steric shielding by the C₆F₅ groups. The overall catalytic performance of **DLA** is thus similar to that of BCF, explained by the stereoelectronic similarity of BCF with the distal reaction center.

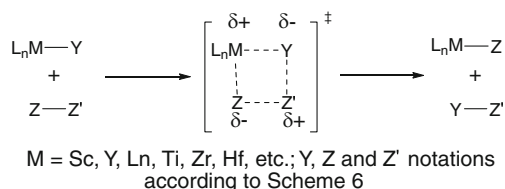
In the following sections the two other cases of strongly polarized XY σ and π bonds activating Z–Z' bonds are discussed by analyzing instructive examples from the literature.



Scheme 12 Dehydrocoupling pathway of ammonia borane (AB)

3.3 Hydrodecoupling and Dehydrocoupling Reactions as Examples of $Z-Z'=H_2$ Activations by Polarized $[X-Y \leftrightarrow X(+)Y(-)]$ σ Bonds of Main Group Element Compounds

As an interesting first activation process induced by highly polarized σ bonded $X-Y$ species, we would like to interpret the relatively complex reaction course of the thermal dehydrocoupling of ammonia borane (AB) in terms of the mechanisms described in Sect. 3. AB thermal dehydrocoupling was recently reviewed in conjunction with the chemical hydrogen storage potential of this molecule (Scheme 12) [8]. The suggested dehydrocoupling pathway of AB operates initially on the basis of step I of Scheme 12, the formal dimerization of 2 equiv. of AB to afford the diammoniate of diborane DADB salt, most probably in the form of a B–H addition reaction. The B–H bond takes the role of a $Z-Z'$ σ bond to be added across the highly polarized B–N σ bond of AB taken as the polarizing $X-Y$ σ bond. This reaction step demonstrates the features of the reversal of an FLP reaction of the σ bonded type I arrangements of Scheme 2. This process is expected to pass through a four-membered cyclic transition state with preceding charge transfer intermediate according to Schemes 6 and 8, emphasizing the high polarity of the bonds. The formed DADB molecule then releases in two dehydrocoupling steps $2H_2$ molecules (step II of Scheme 12) affording a four-membered borazane intermediate. The type of the reaction steps would correspond to the reverse processes of Scheme 6 (top) with H_2 as the eliminated $Z-Z'$ molecule. Following the dehydrocoupling process of AB further, step III of Scheme 9 comes into play, leading to the formation of B-(cyclodiborazanyl)amino-borohydride; mechanistically this step should correspond to a reversed $X-Y$ σ bond FLP type process of Scheme 6 (top). B-(cyclodiborazanyl)amino-borohydride finally isomerizes to cyclotriborazane by an unknown type of mechanism (step IV of Scheme 12). Further multiple hydrogen releases (steps V–VII of Scheme 9) produce borazine in three dehydrogenation steps; mechanistically these are expected to proceed along the lines of the reversal of XY π bond FLP type processes of Schemes 6 and 7 (bottom).



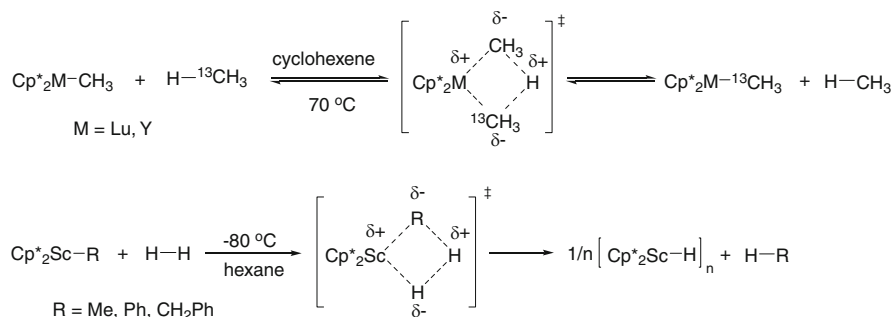
Scheme 13 Sketch of the σ bond metathesis reaction (SBM). Via a four-membered cyclic transition state involving a highly polarized M–Y bond, FLP behavior is demonstrated leading to Z–Z' splitting. M = L_nM complex fragment, Y, Z, Z' = atoms or molecular fragments. Electronegativity of M < electronegativity of Y

3.4 σ Bond Metathesis Reactions as Examples of Z–Z'=H₂ and Alkane Activations by Polarized [X–Y $\leftrightarrow$ X(+)Y[–]] (σ Bonds Applying X = L_nM (L_nM = Transition Metal or Lanthanide Complex Fragment))

σ Bond metathesis (SBM) as sketched in Scheme 13 is an elementary step of organometallic chemistry. It describes the simultaneous σ bond making and breaking of alkyl or hydride complexes of electrophilic, high-valent early transition metals or f-element centers with d^0 or $f^n d^0$ electronic configurations, where oxidative addition or reductive elimination processes can be excluded, since the metal centers do not possess redox properties. These transformations can be envisaged as FLP type reactivity with formation of type **II** arrangements of Scheme 2 or in a more detailed description following a reaction path along Scheme 6. The metal centers contain one or more vacant orbitals acting as “Lewis acidic orbitals” that would provide a low-energy means for the approach of H–H, C–H molecules to be taken as Z–Z' activated species. The M–R bonds had to be taken as the highly polarized X–Y σ type FLP components. Extensive experimental and theoretical studies have shown that the high polarity of the involved L_nM –Y σ bonds enable a low energy $2e^- + 2e^-$ four-centered transition state, and maybe additionally a preceding charge transfer intermediate. In a purely covalent view these transformations violate the orbital symmetry conservation rules (Scheme 13) [9].

One type of reactive L_nM –Y species are the 14-electron complexes of the type Cp^*_2MR (M = Sc, Lu, Y; R = H, alkyl), which can activate both C–H bonds of alkanes and the H–H bond. For instance, degenerate C–H bond exchange with $^{13}CH_4$ is observed with $Cp^*_2M-CH_3$ (M = Lu, Y). It was the first well-characterized example of C–H activation of alkanes by a σ bonded L_nM –Y species (Scheme 14) [10]. The metal center is so highly electrophilic that it can interact with σ -C–H bonds to form an intermediate. The steric bulk of the Cp^*_2M unit prevents quenching of the Lewis acidity by formation of a stable dimer (frustration requirement!).

Later Bercaw and co-workers proposed the concept of σ -bond activation based on systematic work of C–H and H–H bond activation [11]. The hydrocarbyl

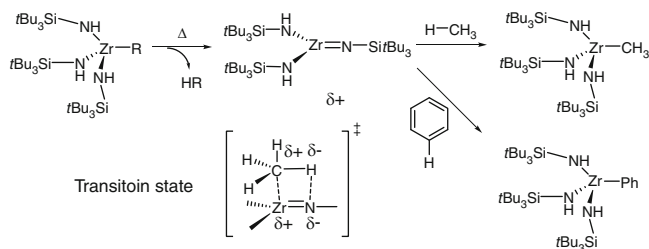


Scheme 14 C–H and H–H bond activation by highly polarized σ bonded $\text{Cp}^*_2\text{M}-\text{R}$ complexes ($\text{M} = \text{Sc}, \text{Lu}, \text{Y}$; $\text{R} = \text{H}, \text{alkyl}$)

derivatives of $\text{Cp}^*_2\text{Sc}-\text{R}$ ($\text{R} = \text{Me}, \text{Ph}, \text{CH}_2\text{Ph}$) also reacted rapidly with H_2 affording $\text{R}-\text{H}$ and the scandium hydride $\text{Sc}-\text{H}$. Quantum chemical calculations based on a model system of $\text{Cl}_2\text{Sc}-\text{H}$ in interaction with H_2 were carried out and revealed the principal character of these reactions related to those of the FLP reactions sketched in Schemes 6 and 7 (top) [12]. However, the calculations have also shown that the nodal plane properties of several vacant scandium d orbitals play an additional supportive role for σ bond metathesis assisting formation of an initial intermediate.

3.5 Amine Borane Reactions as Examples of Z–Z' Activations by Polarized $[\text{X}=\text{Y} \leftrightarrow \text{X}(+)-\text{Y}(-)]$ π Bonds

Reactions of Z–Z' σ bonds with polarized $[\text{X}=\text{Y} \leftrightarrow \text{X}(+)-\text{Y}(-)]$ π bonded systems are rare in the realm of main group element chemistry; at least there is no well-defined example known for low polarity Z–Z' species, such as H–H or C–H bonds, to be converted with the polarized π bonds in a mechanistically established reaction course. Presumably the scarcity of examples may have to do with unfavourable thermodynamics or with the fact that only highly polarized XY π bonds would be capable of Z–Z' activation and such “superpolar” species are not easily available. 1,2-Elimination processes as the reverse reactions of these FLP type π bond activations are however known. One elementary step reaction of this kind was discussed in the context of the ammonia borane dehydrocoupling scheme of Scheme 12.

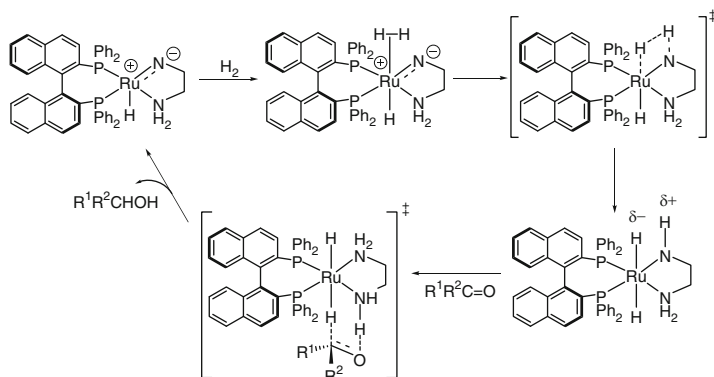


Scheme 15 Methane and benzene activation via the transient $(t\text{Bu}_3\text{SiNH})_2\text{Zr}=\text{NSiR}_3$ complex to be viewed as FLP reactions involving the highly polarized $\text{L}_n\text{Zr}(+)\text{-Nl}(-) \leftrightarrow \text{L}_n\text{Zr}=\text{N}$ bond as $\text{L}_n\text{M}=\text{Y}$ FLP component and the various C-H bonds as Z-Z' σ bond component

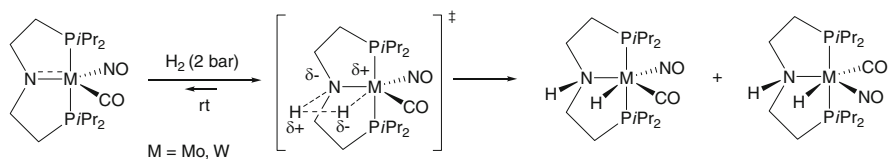
3.6 Examples of Z-Z' σ Bond Activations by Polarized $[X=Y \leftrightarrow X(+)\text{-Yl}(-)]$ π Bonds with $X = \text{L}_n\text{M} = \text{Transition Metal Fragment}$ and $Y = \text{Ligand Group}$

Early L_nM transition metal centers bearing bulky and formally double bonded Y groups ($[\text{L}_n\text{M}=\text{Y} \leftrightarrow \text{L}_n\text{M}(+)\text{-Yl}(-)]$), such as siloxide or silamide ligands, possess inherent electronic unsaturation at the metal center originating from the high electronegativity difference between L_nM and Y. As a consequence, these compounds exhibit surprisingly high reactivity in the activation of methane, representing the so-called “Holy Grail” of C-H σ -bond activation [13]. Wolczanski and co-workers have paved the way with pioneering and fundamental studies on C-H bond activation based on high-valent early d and f block d^0 metals complexes bearing imido ligands with the C-H addition occurring in an FLP type manner across the $[\text{L}_n\text{M}=\text{N} \leftrightarrow \text{L}_n\text{M}(+)\text{-Nl}(-)]$ π bond. For instance, the highly reactive metal imido species $(t\text{Bu}_3\text{SiNH})_2\text{Zr}=\text{NSiR}_3$, which was transiently generated by thermal 1,2-RH elimination from $(t\text{Bu}_3\text{SiNH})\text{ZrR}$, is capable of C-H bond activation of methane and benzene [14]. The reaction captures initially the alkane binding it to the electrophilic, three-coordinate d^0 zirconium center. Then 1,2-C-H addition to the transient $\text{Zr}=\text{N}$ bond follows, as depicted in Scheme 15. The most plausible transition state for such a type of 1,2-RH addition across $\text{M}=\text{Y}$ double bond is a $2e + 2e$ four-membered addition cycle as sketched in generic form in Schemes 2 (arrangement II) and 6 (bottom).

Moving to the right side of the transition metal periodic table, late transition metal imido complexes often also bear polar $\text{M}=\text{NH}-$ moieties of the $[\text{L}_n\text{M}=\text{Y} \leftrightarrow \text{L}_n\text{M}(+)\text{-Yl}(-)]$ π bond type showing cooperativity in the H-H activation and H transfer processes in catalytic hydrogenations, as exemplified by Noyori's chiral ruthenium amido complexes for the catalytic asymmetric hydrogenation of polar unsaturated substrates, such as ketones and imines [15]. The catalytic cycle of the versatile BINAP/diamine-Ru system, which possesses a ruthenium imido hydride key intermediate $(\text{H})\text{Ru}=\text{NH}-$, is depicted in Scheme 16. The ruthenium center adds H_2 followed by H_2 heterolytic cleavage across the $(\text{H})\text{Ru}=\text{NH}-$ π bond affording via



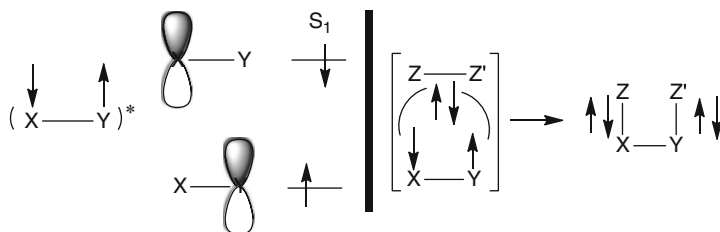
Scheme 16 Noyori type catalysis of the hydrogenation of ketones with H–H bond activation occurring across a $[\text{HRu}=\text{NH} \leftrightarrow \text{HRu}(+)-\text{NH}(-)]$ π bond. This reaction step can be viewed as an FLP activating step as depicted in Scheme 6 (bottom) taking the highly polarized $\text{Ru}=\text{N}$ bond as $\text{X}=\text{Y}$ component and the H–H bond as activated $\text{Z}-\text{Z}'$ σ bonded species



Scheme 17 H–H activation across $\text{Mo}=\text{N}$ or $\text{W}=\text{N}$ bond. This reaction step can be viewed as an FLP activating step depicted in Scheme 6 taking the highly polarized $\text{Mo}, \text{W}(+)-\text{Nl}(-) \leftrightarrow \text{Mo}, \text{W}=\text{N}$ bond as $\text{L}_n\text{M}=\text{Y}$ components and the H–H bond as activated $\text{Z}-\text{Z}'$ σ bond species

a four-membered cycle a $(\text{H})_2\text{Ru}-\text{NH}_2-$ moiety with highly polarized $\text{H}(\delta-)$ and $\text{H}(\delta+)$ bonds to act according to Noyori as a “bifunctional” intermediate. The H–H addition corresponds to an FLP type $\text{Z}-\text{Z}'$ activation process at the highly polarized XY π bonded system of Scheme 6 (bottom). In the catalytic cycle the $(\text{H}_2)\text{Ru}=\text{NH}_2-$ imido moiety then reacts further, functioning as hydrogen donor with double H transfer to a polar $[\text{X}=\text{Y} \leftrightarrow \text{X}(+)-\text{Yl}(-)]$ π bonded organic systems passing through a six-membered transition state related to a double H transfer step to be discussed in Sects. 6 and 7.

Recently our group has prepared a series of middle transition metal $\text{Mo}(0)$ and $\text{W}(0)$ amido complexes $\{\text{M}(\text{NO})(\text{CO})(\text{PNP})\}$ ($\text{M} = \text{Mo}, \text{W}$, $\text{PNP} = (i\text{Pr}_2\text{PCH}_2\text{CH}_2)_2\text{NH}$), which were found to activate the H–H bond. This reaction can also be viewed as an FLP reaction with the highly polarized $[\text{Mo}, \text{W}(+)-\text{Nl}(-) \leftrightarrow \text{Mo}, \text{W}=\text{N}]$ bonds as $\text{L}_n\text{M}=\text{Y}$ components (Scheme 6) and H_2 as the $\text{Z}-\text{Z}'$ component (Scheme 17) [16]. The $\text{M}=\text{N}$ partial double bond character was evidenced by X-ray diffraction studies showing $\text{M}-\text{N}$ separations shorter than those of the metal amino precursors, but longer than those expected for $\text{L}_n\text{Mo}, \text{W}=\text{N}$ double bonds in accord with the idea of highly polarized bonds. Indeed a $2e + 2e$ four membered cycle is assumed to be involved as a charge transfer



Scheme 18 S_1 excitation of a strongly polarized XY double bond and demonstration of spin conservation in the transformation of the excited XY species with a $Z-Z'$ σ bond molecule

intermediate and/or in the transition state. The H–H split “bifunctional” species with highly polarized Mo,W–H(δ^-) and NH(δ^+) bonds are highly active catalysts for imine hydrogenation, transferring the polar H atoms most probably via double H transfers with six-membered cycles as depicted in generic form in Scheme 18 (bottom).

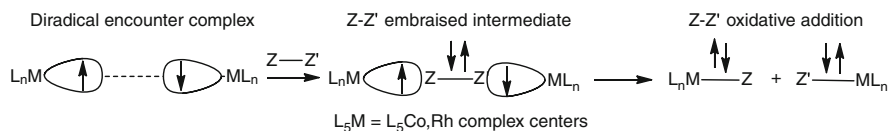
4 Perspectives for Type I–III FLP Activation by Electronic Excitation

$S_0 \rightarrow S_1$ excitations of Stephan type FLPs, $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ excitations of the XY polarized σ and π bonds, respectively, appear to be a principal alternative for the activation of ZZ' molecules to undergo 1,2-addition to the XY species. The $\sigma \rightarrow \sigma^*$ excitations are expected to be of highest energy in the given series of FLPs, thus reducing the feasibility of application of these activating systems.

In the following we exemplarily elaborate on the photochemical activation pathway of $Z-Z'$ molecules in the presence of a highly polarized $[X=Y \leftrightarrow X(+)-Y(-)]$ π bonded molecular systems. Via excitation the charge separation of the ground state becomes partly or even completely lifted by equal single occupancy of orbitals located prevalingly at the X and Y centers (Schemes 6, 7, and 8). Subsequent to the $S_0 \rightarrow S_1$ excitation, the $(XY)^*$ system is then expected to interact with the $Z-Z'$ σ bonded molecules inducing facile transformations along a photochemically allowed $2e + 2e$ process (Scheme 18).

This photochemical pathway of σ bond activation resembles those of established thermal H_2 or C–H additions involving the ground state (S_0) of dinuclear face-to-face square pyramidal Co(II) or Rh(II) type encounter complexes with antiferromagnetically coupled spins (Scheme 19) [17–19].

One precondition for a thermally excited process is that the corresponding absorptions should be located in the NIR. Stephan type FLPs are normally combinations of strong Lewis acids with the Lewis acidic orbital at low energies and strong Lewis bases with the Lewis basic lone pair orbital at relatively high energies. The resulting relatively small HOMO/LUMO gaps are however normally

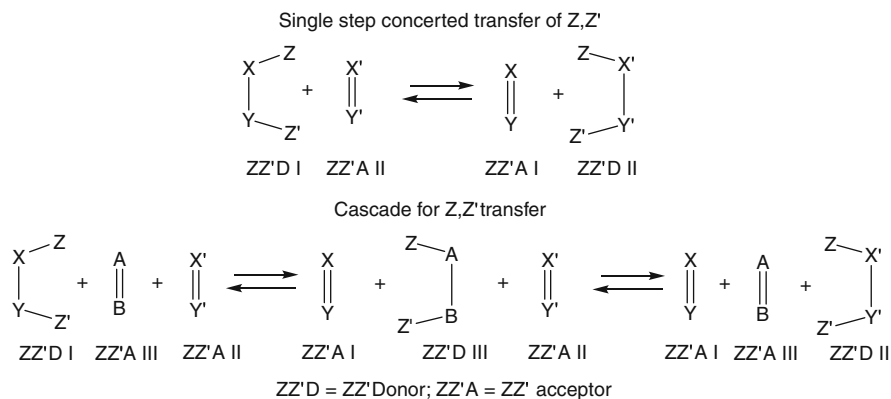


Scheme 19 Schematic sketch of the take up and splitting of σ bonded $Z-Z'$ molecules by antiferromagnetically coupled diradical dinuclear Co,Rh(II) centers (S_0 state) following an oxidative addition pathway

still not in the energetic range accessible for thermal excitation. As mentioned before the LUMO of the “standard” type Lewis acid $B(C_6F_5)_3$ (BCF) of Stephan type FLPs would be at -3.81 eV, while the HOMO of the exemplary Lewis bases tetramethylpiperidine or tri(*tert*-butyl)phosphine would be at -5.22 and -5.41 eV, respectively, displaying HOMO/LUMO gaps of 1.41 and 1.60 eV (32.5 and 36.9 kcal/mol), truly not in the range of thermally accessible energies. In addition, so-called linked FLPs with rigid backbones are often highly colored with charge transfer absorptions in the visible range [20, 21]. The idea of a diradical activation mode of FLPs with thermally induced formation of charge transfer complexes is still a challenge in the field. The possibility for realization of this idea might however get support from peculiar experimental observations of thermally strongly enforced FLP reactions. Several Stephan type FLPs react to split H_2 only at elevated temperatures. For instance, the pair of BCF and anilines react at $110^\circ C$ [22], the DLP/imine pairs at $120^\circ C$ [4–7] (Sect. 3.1), and BCF/amine pairs published by Repo et al. [23–26] react only at $110^\circ C$. These observations would contradict the necessity of kinetically relevant equilibrium concentrations for FLP formation due to the fact that elevated temperatures disfavour the FLP association. Therefore we would like to propose that in these cases the higher temperatures can induce the thermal excitation of the FLPs into the S_1 states of the formed charge transfer complexes, thereby counteracting the FLP equilibrium concentration effect.

5 General Aspects of Z, Z' Double Atom or Group Transfers Between Highly Polarized Double Bonds of XY and $X'Y'$ Molecules by Combined Elimination and Addition Processes

Z, Z' double atom or group transfers between double bonds of XY ($ZZ'A$ II) and $X'Y'$ ($ZZ'D$ II) molecules can be viewed as combined 1,2-elimination and 1,2-addition processes, following concerted σ bond transformations such as the generic reaction courses of Scheme 20. They may appear as a single step double ZZ' transfer [Scheme 20 (top)] or as a series of combined double ZZ' transfers called a transfer cascade [Scheme 20 (bottom)]. In the transfer cascade the $AB/ZABZ'$ acceptor/donor system ($ZZ'A$ III/ $ZZ'D$ III) could take the function as a catalyst for the double ZZ' transfers between the polarized double bonded systems of XY and $X'Y'$.



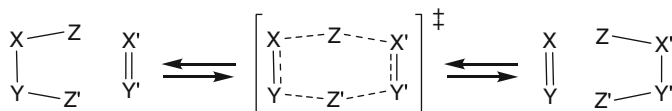
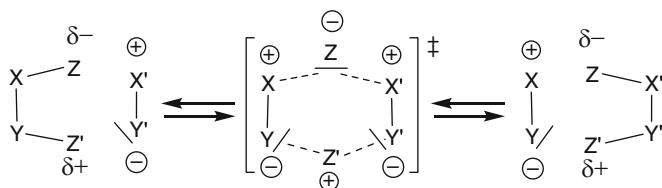
A,B,X,Y and X',Y' = atoms or molecular fragments of main group and transition elements

Scheme 20 Generic schemes of double H transfer reactivity. *Top*: concerted Z,Z' double atom or group transfers between the double bonded systems of XY (ZZ'A II) and X'Y' (ZZ'D II). *Bottom*: combined double ZZ' transfers are called transfer cascade. In the transfer cascade the AB/ZABZ' acceptor/donor system (ZZ'A III/ZZ'D III) could take the function as a catalyst for the double ZZ' transfers between the double bonded systems of XY and X'Y'.

The homopolar variant of the concerted double H atom transfer according to Scheme 20, Pathway 1 seems not to work in reality. These conversions, like the degenerate exchange of two hydrogen atoms between ethane and ethylene, are expected to be feasible reactions because they correspond to symmetry allowed $2e + 2e + 2e$ electrocyclic processes. However, practical examples of such reactions with non-polar reactants are not operative at temperatures below 200–300 °C and thus contradict the orbital conservation rules. There is surprisingly low tendency for concerted double H atom transfer reactions [27–30].

Apparently these reactions are getting more feasible under circumstances related to those of polar Z,Z' atom or group transfers involving polarized π bonded species of the $[\text{X}=\text{Y} \leftrightarrow \text{X}(+)-\text{Y}l(-)]$ or $[\text{X}'=\text{Y}' \leftrightarrow \text{X}'(+)-\text{Y}'l(-)]$ type according to Sect. 2.2. Thus, the polar Pathway 2 of Scheme 21 seems to be of much lower activation barrier than that of Pathway 1.

In this chapter we would like to emphasize the description of Pathway 2 of Scheme 21 further demonstrating the feasibility of polar reaction courses. Viewing such processes in their most extreme polar form with total charge separations at the XY and X'Y' double bonds, one could consider the Z and Z' atom or group transfer as $[\text{Z}]^-$ anionic and $[\text{Z}']^+$ cationic transfers as depicted for the transition state of Pathway 2 of Scheme 21. Such very polar transfers are often seen to have very low activation barriers. For instance, when Z and Z' refer to H atoms, one would consider combined (and concerted?) proton and hydride transfers, which are in separate forms naturally occurring facile processes, indeed in most cases low activation barriers. $[\text{Z}]^-$ and $[\text{Z}']^+$ transfers between polarized $\text{X}(+)-\text{Y}l(-)$ and $\text{X}'(+)-\text{Y}'l(-)$ double bonds may occur simultaneously or nearly simultaneously, but also stepwise with the order of $[\text{Z}]^-$ before $[\text{Z}']^+$ or $[\text{Z}']^+$ before $[\text{Z}]^-$. Pathway 2 of Scheme 21 thus separates the six

Pathway 1: non-polar $X=Y$ and $X'=Y'$ substrates

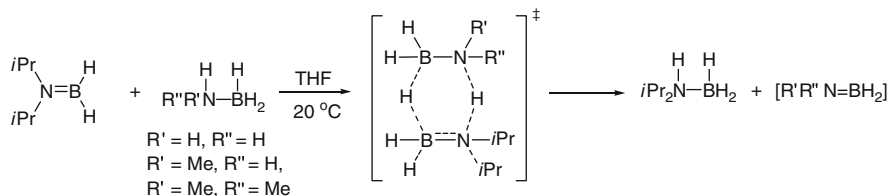
Pathway 2: polar substrates

Scheme 21 Generic scheme for Z,Z' group transfers between non-polarized (Pathway 1) and strongly polarized π bonded systems (Pathway 2). $X, Y, X', Y', Z, Z' =$ atoms or molecular fragments. For Pathway 1: electronegativity of $X, X' \cong$ electronegativity of Y, Y' . For Pathway 2: electronegativity of $X, X' <$ electronegativity of Y, Y' ; as a consequence Z is expected to bear a high δ^- charge and Z' a high δ^+ charge in the transition state. In a first approximation Pathway 2 can be separated into simultaneous transfer processes: $Z(-)$ from X to X' and $Z'(+)$ from Y to Y'

electron process of Pathway 1 into a two electron $[X \cdots Z \cdots X']^+$ and a four electron $[Y \cdots Z' \cdots Y']^-$ process. Again, as for the $Z-Z'$ addition/elimination reactions, the strongly polar reaction mode seems to be preferred over the homopolar covalent transformation course. It should be mentioned at this point that polar cascade Z,Z' transfer reactions of Scheme 21 are expected to follow the same principles as those just described for the polar concerted ZZ' transfer reactions.

6 Metal-Free H_2 Addition and Elimination Reactions as Examples of the General Case of ZZ' Additions/Eliminations and Double H Atom Transfer Processes Involving Highly Polarized XY and $X'Y'$ Double Bonded Species

In this section and Sect. 7 that follows we will demonstrate the proof of the given concepts of ZZ' σ bond activations presenting mainly examples of well-studied 1,2-additions or 1,2-eliminations and double atom or group transfer processes involving $Z-Z'=H-H$ and $C-H$ bonds. The polarized XY and $X'Y'$ double bonded species covered in this section are restricted to $Z-Z'=H-H$ and main group compounds (“metal-free”) excluding transition metal containing units. Based on $Z,Z'=H$, 1,2-addition processes are denoted as hydrogenations and, vice versa, 1,2-elimination processes are denoted as dehydrogenation processes. Double Z,Z' transfers applied to H atom transfers between XY and $X'Y'$ are denoted as transfer hydrogenations.



Scheme 22 Metal-free transfer hydrogenation of $iPr_2N=BH_2$ with an amine borane as a hydrogen donor. Double H transfer for $Z, Z'=H$, H transfers between strongly polarized XY and $X'Y'$ double bonded species along Pathway 2 of Scheme 21 (X, Y, X', Y', Z, Z' = atom or molecular fragments)

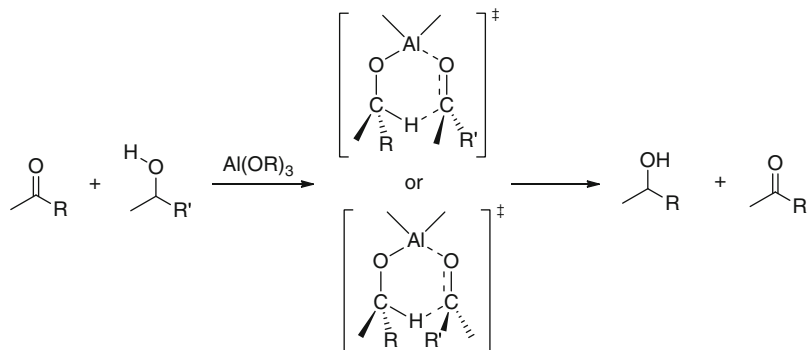
6.1 Metal-Free Hydrogenations/Dehydrogenations with $Z-Z'=H_2$ as σ Bond Activation Reactions: Main Group Element Processes

6.1.1 Hydrogen Transfer Between Amine Boranes

Very recently the group of Manners has reported an unexpected metal-free hydrogen transfer between amino boranes and amine boranes (Scheme 22) [31, 32]. The polarized $iPr_2N=BH_2$ monomeric species, which is stabilized by bulky iPr substituents, acts as a hydrogen donor and reacts with the hydrogen donor ammonia borane (**AB**) to afford the hydrogenated product $iPr_2NH \cdot BH_3$ along with the dehydrogenation product $[NH_2-BH_2]_n$. The reaction can be carried out in either sealed or open systems with no effect on products, confirming the “gas-free” nature of the transfer hydrogenation by direct and concerted hydride and proton transfer from **AB** to $iPr_2N=BH_2$ instead of a reaction path via initial H_2 release from **AB** followed by H_2 addition to the unsaturated $B=N$ double bond of $iPr_2N=BH_2$. Based on the polarized nature of $B-N$, $B=N$, $B-H$, and $N-H$ bonds, such a transfer hydrogenation reaction presumably proceeds via the $2e^- + 2e^- + 2e^-$ electrocyclic transition state related to that described as Pathway 2 in Scheme 18. The generality of the reaction was validated by using other double H transfer sources such as $MeNH_2 \cdot BH_3$ or $Me_2NH \cdot BH_3$. This facile, room temperature hydrogenation of $B=N$ bonds of amino boranes is of fundamental significance and has potential implications for the regeneration of amine borane hydrogen storage materials.

6.1.2 Meerwein–Pondorf–Verley Reductions Understood as Double H Transfer Reactions

σ Bond activation by double group transfer between $[X=Y \leftrightarrow X(+)-Y(-)]$ and $[X'=Y' \leftrightarrow X'(+)-Y'(-)]$ π bonded systems constitutes the mainly aluminum alkoxide mediated Meerwein–Pondorf–Verley reduction of ketones, which may



Scheme 23 Schematic sketch of the Meerwein–Pondorf–Verley reduction (MPV)

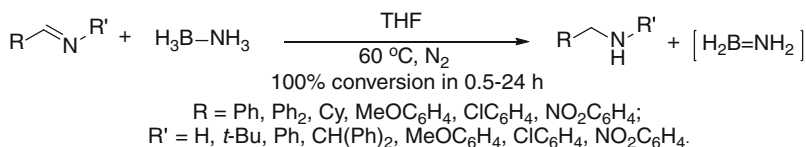
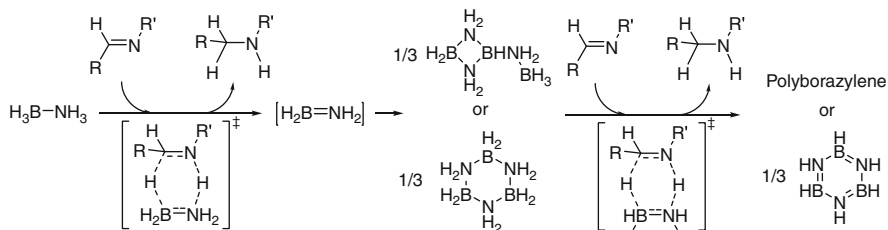
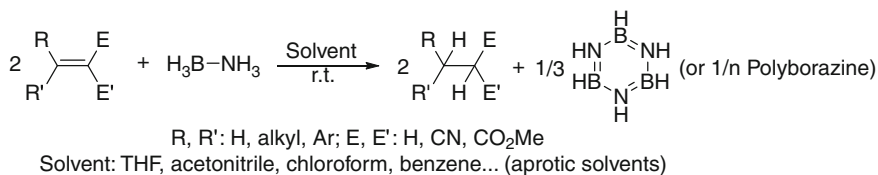
also be carried out in an enantioselective fashion [33–35]. The hydrogen transfer proceeds via a six-membered transition state, as depicted in Scheme 23. The given type of transition states resemble closely the generic mechanism proposed in Scheme 21 (bottom) for polar Z, Z' atom or group transfers involving polarized π bonded species with $[Z']^+ = [AlR_2]^+$ and $Z^- = H^-$.

6.1.3 Concerted or Stepwise Main Group Element Transfer Hydrogenations Between Ammonia Borane and Polarized π Bonded Species

By mechanistic means double Z, Z' group transfers between $[X=Y \leftrightarrow X(+)-Yl(-)]$ and $[X'=Y' \leftrightarrow X'(+)-Y'l(-)]$ π bonded systems may be concerted single-step processes or multi-step processes. The multi-step processes often appear as cascades of coupled double Z, Z' transfers. Transfer hydrogenations where Z, Z' correspond to H atoms and their transfers between polarized π components involve “bifunctional” or bipolar H atom transfers with polarized $H(\delta-)$ and $H(\delta+)$ atom transfers. The “bifunctional” hydrogenation chemistry indeed shows great preference for polarized XY and $X'Y'$ double bonded substrates (preferably organic carbonyl compounds and imines, and strongly polarized substituted olefins). Single-step or multi-step transfer hydrogenations with main group element compounds are denoted as “metal-free.” Amine boranes are the most versatile “bifunctional” polar reagents in transfer hydrogenations, because of their high difference in partial charges of the transferred H atoms.

Amine Boranes as Hydrogen Donors of Transfer Hydrogenations

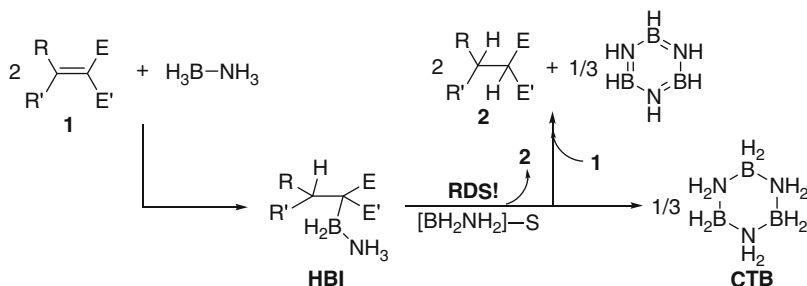
Ammonia–borane (H_3N-BH_3 , **AB**), the hydrogenated form of a highly polarized $[X=Y \leftrightarrow X(+)-Yl(-)]$ $B=N$ double bonded species, is considered a feasible hydrogen donor component for a double H transfer to polar $[X'=Y' \leftrightarrow X'(+)-Y'l(-)]$ species to yield typically $H(\delta-)-X-YH(\delta+)$ polar products along Pathway 2 of Scheme 24.

**Scheme 24** Metal-free transfer hydrogenation reactions of **AB** with various imines**Scheme 25** Concerted double H transfer mechanism for the metal-free transfer hydrogenation of imines by **AB** showing two stages of double H transfers from amine boranes to imines. Hydrogen donor atoms in *red*, hydrogen acceptor atoms in *blue***Scheme 26** Metal-free transfer hydrogenation reactions of **AB** with polarized olefins at room temperature

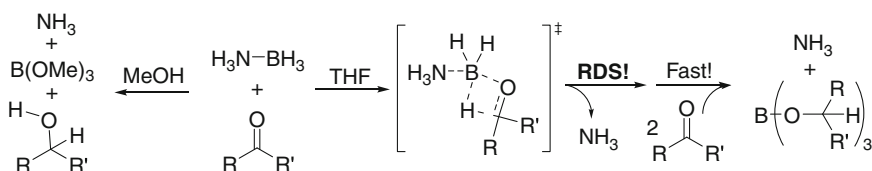
In our group we have successfully applied the C=N double bond of imines as polar hydrogen acceptor compounds. Imines could be transfer hydrogenated by **AB** under mild conditions without the presence of a catalyst (Scheme 21) [36] with the corresponding amine as the sole product.

However, the reactions were complicated by dehydrocoupling processes of the $[\text{H}_2\text{N}=\text{BH}_2]$ intermediate as shown in Scheme 25; in this case the reactions were similar but also different and more complex than in the thermal ammonia borane dehydrogenation described in Scheme 9. Deuterium labeling experiment using selectively deuterated **AB** derivatives, NH_3BD_3 (**AB(D)**), ND_3BH_3 (**A(D)B**), and ND_3BD_3 (**A(D)B(D)**), confirmed the regio-selectivity that H_B went to the C terminal and H_N went to the N terminal of the C=N double bond, respectively.

Highly polarized olefins substituted with two electron-withdrawing groups (EWGs, $-\text{CN}$ or $-\text{CO}_2\text{Me}$) on one terminal of the C=C double bond can also be reacted with **AB**. In this case, metal-free transfer hydrogenation proceeded rapidly even at room temperature (Scheme 26) [37, 38]. When a protic solvent like methanol was used, the olefin could be transfer hydrogenated rapidly at room



Scheme 27 H_B before H_N transfer pathway for the transfer hydrogenation of **AB** with polarized olefins through a hydroboration intermediate (**HBI**)



Scheme 28 Metal-free reduction of carbonyl compounds by **AB**

temperature, although with accompanying solvolysis of **AB** instead of its dehydrocoupling transformation [39].

Again, deuterium labeling studies carried out in acetonitrile demonstrated the exclusive regio-selectivity that the H_N atoms went to the EWG terminal of the C=C double bond and the H_B atoms went to the other C terminal. The double H transfer went stepwise with formation of a hydroboration intermediate (Scheme 27, **HBI**). **HBI** was trapped and characterized by low temperature NMR, clearly stating that the transfer of the hydridic H_B happened before the RDS, while the transfer of the protic H_N occurred during the RDS. The intermediacy of [NH₂=BH₂] was proved by addition of cyclohexene into the reaction mixture, where Cy₂B-NH₂ was identified as the trapping product [40]. Formation of the final boron compounds borazine and polyborazine follows grossly dehydrocoupling of solvent stabilized [NH₂=BH₂] rather than dehydrogenation of **CTB** (cf. Scheme 9).

In these series of transfer hydrogenation reactions with ammonia, borane carbonyl containing compounds, such as ketones and aldehydes, were also reacted with **AB** without the presence of a catalyst in the metal-free reaction mode. Hydroboration reactions were observed in an aprotic solvent like THF and transfer hydrogenation in a protic solvent like methanol (Scheme 28) [37]. When methanol was used as the solvent, metal-free methanolysis of **AB** took place, with the carbonyl compounds being hydrogenated by formal H⁻ and H⁺ transfers. Nevertheless, it became clear that in the reduction of these C=O containing compounds by **AB** a stepwise reaction mode was followed and not a concerted one as in Scheme 21, Pathway 2. These reactions of ketones and aldehydes with ammonia borane (**AB**) thus proceeded with H⁻ before H⁺ or H(δ⁻) before H(δ⁺) transfers.

Transfer hydrogenations involve overall exchange of two hydrogen atoms between two hydrogen donor/acceptor pairs and coupling of a hydrogenation with a dehydrogenation process. In the realm of main group element chemistry these may be single-step or multi-step. Single-step processes are in most cases concerted double H transfers, but they may switch over to stepwise H transfers in the case where the H accepting substrate gets more electrophilic.

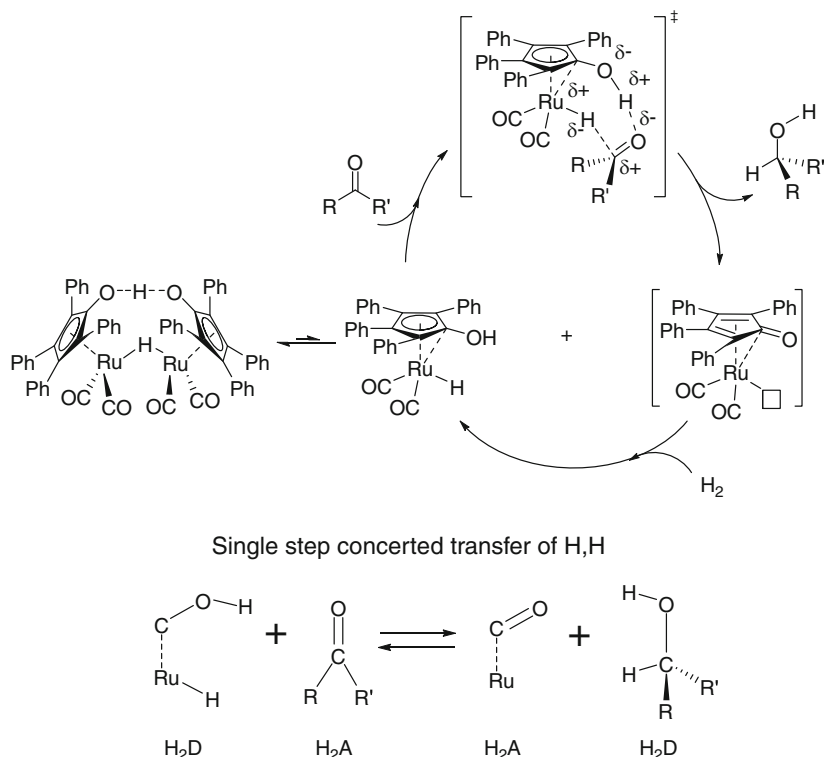
6.2 Transition Metal Based Shvo Type Hydrogenations

Shvo's catalyst, a diruthenium bridging hydride, utilizes electronically coupled acidic and hydridic hydrogens to catalyze efficiently the hydrogenation of polarized CC double and triple bonds [41–43]. The dimeric precatalyst is in equilibrium with a monomeric reducing hydroxycyclopentadienyl hydride as hydrogen donor and an unsaturated oxidizing dienone dicarbonyl species as hydrogen acceptor, both being involved in the catalytic cycle. Detailed mechanistic studies based on low-temperature kinetics and kinetic isotope effects indicated a concerted second-coordination-sphere mechanism involving simultaneous transfer of hydride from ruthenium and proton from the C_5H_4OH group (Scheme 29) [44–46] although a primary coordination sphere mechanism has also been envisaged. From a systematic point of view the catalytic cycle is not fully in line with the mechanistic picture of double H transfers of generic Scheme 21, Pathway 2 since, as detailed in the bottom scheme of Scheme 29, the $H-Ru\cdots C-O-H$ unit is spaced by one more atom than the $HX-YH$ unit of Scheme 21. Nevertheless the analogy holds in the sense that all the atoms of the $Ru\cdots C-O-H$ unit are electronically coupled.

7 Transition Metal-Based Transfer Hydrogenations with Double H Transfers or Double H Transfer Cascades: H_2 Transfer Between XY and X'Y' Highly Polarized π Bonded Molecules and Eventually Polarized $L_nM=Y$ Species (L_nM = Transition Metal Fragment)

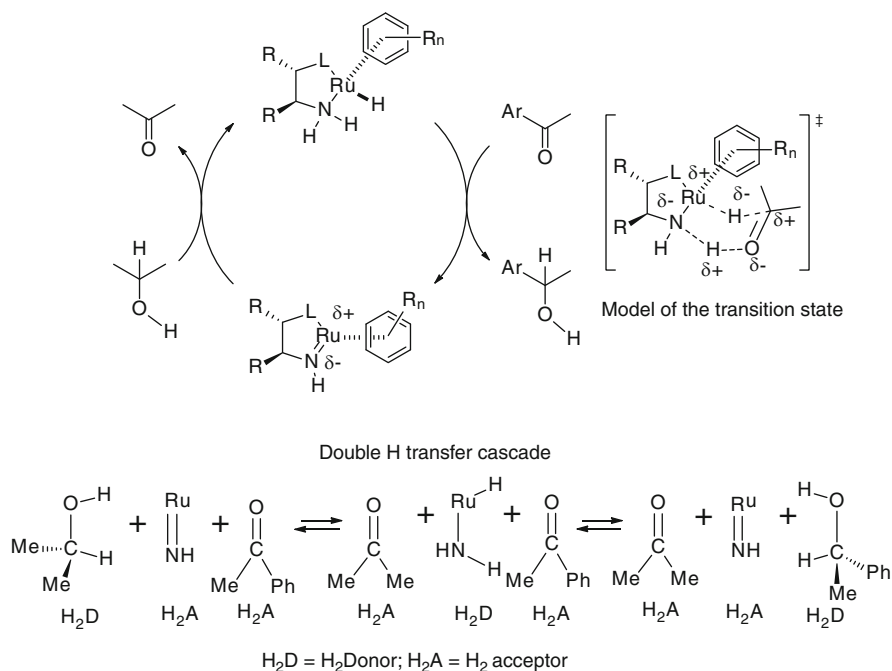
7.1 Noyori Type Transfer Hydrogenations as Cascade Type Double H Transfers

In previous sections it has been mentioned that the groups of Noyori, Morris, and recently of Milstein had explored the prototype of Ru-H/NH bifunctional catalysts for highly efficient achiral and asymmetric hydrogenations [47–49]. In conjunction



Scheme 29 Shvo's catalyst and catalytic cycle for the hydrogenation of ketones showing the crucial double H transfer step as transition state of the catalytic reaction course

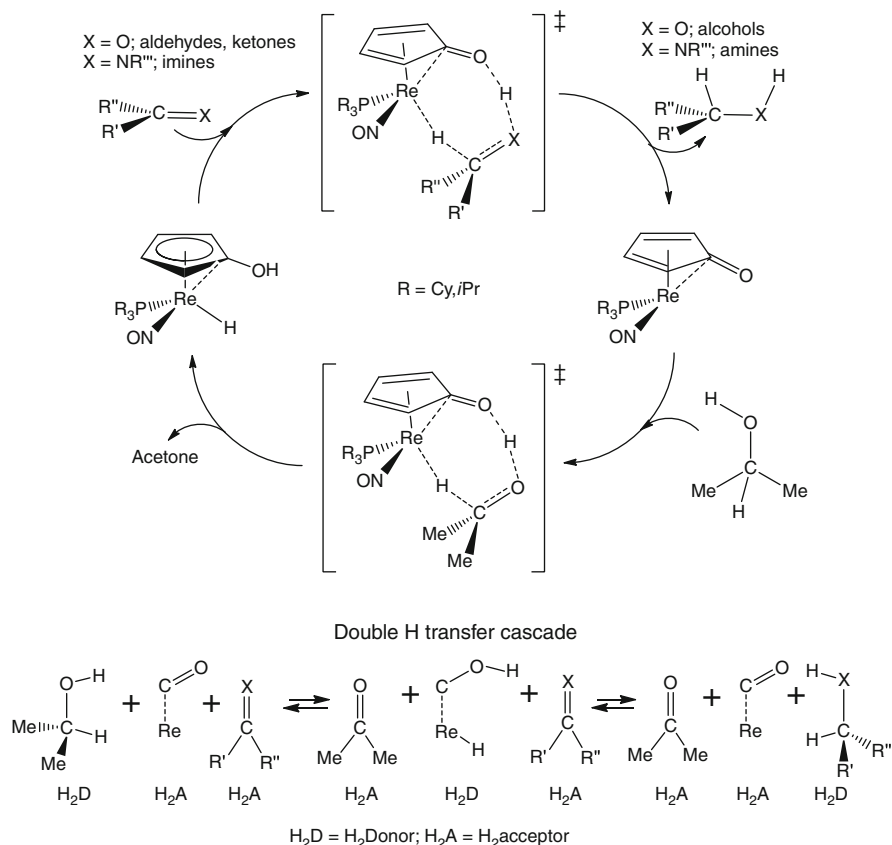
with these reactions, transfer hydrogenation of ketones and imines were studied, showing enormous catalytic activities with turnovers per hour of over a million [50–52]. The real catalytic species of these reactions was identified later on and found to be related to those of hydrogenation catalyses, the unsaturated 16-electron metal amido complex with highly polarized $\text{HRu}(+)\text{--Ni}(-)\text{H} \leftrightarrow \text{HRu}=\text{NH}$ bonds serving as central double H transfer intermediates. These $\text{L}_n\text{M}=\text{Y}/\text{L}_n\text{MH}=\text{YH}$ metallo components mediate the double H transfer process between the XY/HXYH and $\text{X}'\text{Y}'/\text{HX}'\text{Y}'\text{H}$ components of the generic Scheme 21, presumably via a concerted sequence of steps of the cascade type as proposed in Scheme 20 (bottom) and as demonstrated in the transfer hydrogenation mechanism proposed in Scheme 30.



Scheme 30 Noyori/Ikariya/Murata type catalyst for the transfer hydrogenation of ketones using isopropanol as a hydrogen donor [53]

7.2 Shvo Type Transfer Hydrogenations of the Cascade Type Double H Transfers

An attempt to develop active rhenium catalyst based on the principles of Shvo's catalysis isoelectronic replacement of the hydridic moiety of $\text{H}-\text{Ru}-\text{CO}$ with the $\text{H}-\text{Re}-\text{NO}$ unit has been anticipated [54]. The new type of hydroxycyclopentadiene $\text{Re}(\text{I})$ nitrosyl complexes $[\text{Re}(\text{H})(\text{NO})(\text{L})(\text{C}_5\text{H}_4\text{OH})]$ ($\text{L} = \text{PCy}_3, \text{P}t\text{Pr}_3$) are active catalysts in the transfer hydrogenation of ketones and imines using 2-propanol as solvent and as H_2 donor [Scheme 31 (top)]. Interestingly and in contrast to Shvo type complexes, the rhenium bifunctional complex showed partial isomerization to the *trans* dihydride cyclopentadienone species of the type $[\text{Re}(\text{H})_2(\text{NO})(\text{L})(\text{C}_5\text{H}_4\text{O})]$, as yet untypical in the realm of bifunctional catalysis apparently expressing the extraordinary strength of $\text{Re}-\text{H}$ bonds. DFT calculations suggested a secondary-coordination-sphere concerted mechanism of the cascade type generic reaction of Scheme 20 (bottom), with the acidic proton $-\text{OH}$ and the hydridic hydrogen of $\text{Re}-\text{H}$ as transferred hydrogen atoms. The cyclopentadienone intermediate as hydrogen acceptor molecule was trapped by addition of pyridine, further supporting the catalytic cycle.

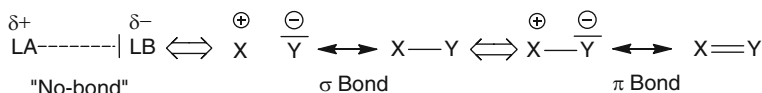


Scheme 31 Shvo type rhenium based transfer hydrogenation catalysis (*top*) following a cascade type mechanism (*bottom* scheme)

Again, as in the case of the reaction of section 6.2, this cascade Shvo type transfer hydrogenation does not, in a strict sense, fully obey the requirements of the generic double H scheme of Scheme 20 (bottom), since as Scheme 31 (bottom) demonstrates, the doubly bonded essential Re species does not consist of just two atoms but rather spaced by one more carbon atom. Apparently this “flaw” has no consequence to the functional model.

8 Conclusions

In this chapter it has been demonstrated that Lewis acid and base functions coexist in the form of non-bonded Stephan type FLPs, highly polarized σ and π bonds:



These species can activate and heterolytically split generic Z–Z' σ bonds of low polarity (H–H and C–H). In addition this chapter has reviewed the double H transfer reactions between two highly polarized π bonded species related to the σ bond activation case of polarized π bonds. The highly polarized nature of bonds may completely change reaction profiles and lead to reaction courses, which are not accessible by purely covalent bond transformations and forbidden by the orbital conservation principle.

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Frustrated Lewis Pairs II

Expanding the Scope

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